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(54) Title: IMPROVED LASER GROOVING AND DOPING METHOD

(57) Abstract

A method of simultaneous laser grooving, cleaning and doping of silicon material is achieved by using a laser scriber to scribe grooves in the silicon surface, in a mixture of Cl_2 and BCl_3 as ambient gas. The addition of BCl_3 to the ambient does not interfere with the removal of the silicon ejected during scribing by reaction with chlorine.

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IMPROVED LASER GROOVING AND DOPING METHOD

Introduction

The present invention relates generally to the art of semi-conductor device manufacture and in particular the invention provides an improved method of groove formation and doping using laser scribing.

Background of the Invention

Certain electronic devices such as solar cells make advantageous use of buried contacts in which a doped groove is filled with metal contact material to provide an efficient contact structure. Prior art methods of producing buried contacts involve a large number of steps including:

a) forming a top surface junction and an overlying oxide layer;

b) scribing grooves in the surface of the oxide layer and the underlying semi-conductor material using a laser scriber usually in an air or inert gas environment;

c) cleaning the grooves with an etchant such as sodium hydroxide to remove debris from the grooves and the top surface of the cell;

d) applying a dopant material to the surfaces of the grooves either by chemical vapour deposition or by use of a spin on dopant substance;

e) high temperature processing to drive the dopant into the surface of the cell typically at 1000°C or greater;

f) removal of boron glass deposits formed during the doping procedure;

g) formation of metal contacts in the grooves.

It will be appreciated that in certain device types such as bi-facial solar cells, where different doping types are required in different contact grooves, the above sequence would have to be repeated more than once, possibly with additional mask application and removal steps

As well as being a lengthy process this procedure includes a high temperature step typically carried out at 1000° or greater and which is not compatible with some semi-conductor fabrication technologies, making it impossible to use this grooving technique in conjunction with these technologies. It is also well known that the cost of production of semi-conductor devices is closely related to the number of processing steps involved and therefore it is highly desirable to avoid processes which include a large number of steps. The above process has been in use for a number of years and to date no suitable improvement has been devised.

Typically, when laser grooves have been formed in semi-conductor devices it has been done with an infra-red laser travelling over the surface of the device at a relatively high speed. In this process, the laser beam penetrates deeply into the surface of the device causing heating of the silicon well below the surface with the result that a well of molten silicon is formed. As boiling takes place in the lower regions of the well the silicon in the well is forced out of the resultant groove and thrown up into the ambient atmosphere. Typically, the silicon thrown out of the groove is oxidised and debris is scattered around the area of the groove with some debris remaining inside the groove itself. Such grooves resulting from laser scribing are not in a suitable state for further processing and must be cleaned , typically using a sodium hydroxide etchant, to remove unwanted oxidised silicon particles scattered within and around the groove. This etching step must be done carefully to avoid removal of all of the top surface oxide.

It is also known to perform precision laser etching in a reactive gas environment where silicon is removed from a surface in very small incremental quantities of, for example, one cubic micrometer by a highly focused and accurately positioned laser beam which effectively melts a small volume of silicon. As this processing is done in a reactive gas atmosphere, such as chlorine, the silicon reacts with the chlorine to form volatile products thereby causing a very clean etch to occur. Due to the limited power output of readily available laser systems and the desire for high resolution etching the melting must be done in very small incremental volumes. Consequently, this process is very slow and would not be suitable for mass production of large area devices. Using this process it might be possible to produce a groove at the rate of in the order of half a millimetre per second, which is much too slow for large scale commercial production of devices requiring some hundreds of metres of grooves per module. By comparison lasers capable of scribing grooves in silicon at up to 500mm per second are currently employed in the manufacture of existing laser grooved solar cell devices.

It is also known that lasers can be used to heat the surface of a solar cell without melting to drive dopant into the surface for junction formation and prior art arrangements are also known in which high quality sharp cut-off junctions are formed by using an ultra-violet laser having low penetration into the silicon surface to melt the surface to a depth of up to a few hundred

nanometres in a dopant gas environment such that the dopant atoms are absorbed into the molten silicon but do not penetrate into the solid silicon below. Such techniques have only ever been used on flat surfaces and are considered inappropriate for grooved surfaces where the wall of the groove might be difficult to illuminate uniformly for uniform melting and doping.

Laser grooving and simultaneous doping was attempted previously by Pirozzi *et al.* (1995) using a gaseous ambient of pure PCl_3. In this system, however, there was no mechanism by which silicon ejected from the groove by the laser was removed or otherwise prevented from contaminating the wafer surface. The window through which the laser illuminates the silicon and behind which the gas is contained might also become contaminated and so the process may need to be interrupted to clean the window. Pirozzi *et al.* used a "light chemical treatment" to remove melted residues after scribing at 532 nm. Such a treatment, if applied to the simultaneously doped grooves, might pinhole or remove entirely the groove wall diffusion. The Pirozzi paper contains no evidence that the attempted simultaneous grooving and doping was successful.

Summary of the Invention

According to a first aspect the present invention provides a method of forming grooves in a semiconductor substrate or a layered semiconductor material arranged to accept buried contacts, wherein a substrate or layered semiconductor material to be grooved is held in a reactive gas environment at least during a grooving process and a laser beam is directed over the surface of the substrate or layered semiconductor material to cut a groove in the substrate or layered semiconductor material, the gas pressure, laser wavelength, laser scan rate and peak laser power being selected to optimise groove shape and minimise the amount of debris on surfaces of the substrate or layered semiconductor material and in the groove after scribing.

According to a second aspect, the present invention provides a method of forming grooves through all of one or more semiconductor layers formed on a substrate without significant damage to the substrate, wherein the substrate carrying the layers to be grooved is held in a reactive gas environment at least during the etching process and a spot focused laser beam is directed over the surface to cut a groove in the semiconductor layers, the laser wavelength being selected to be strongly absorbed by the semiconductor layers and weakly absorbed by the substrate and laser scan

rate and the gas pressure and peak laser power being adjusted to optimise groove formation to control the shape of the groove and amount of debris remaining on the surfaces of the substrate and in the groove after scribing.

Preferably, the reactive gas responsible for consuming the ejected silicon is a halogen and more preferably chlorine.

Preferably, the laser will be a Nd:YAG laser focused to a spot on the surface to be grooved. The substrate will be translated relative to the beam. Other configurations, however, are also possible including high power excimer lasers line focused to form lengths of groove before being stepped to a new location over the material to be grooved.

Experimental work has been performed with a Nd:YAG laser providing 1064 nm and 532 nm wavelength light and pumping powers of 1.8-kW. It is anticipated, however, that light of other wavelengths such as 193 nm, 248 nm, 355 nm, 690 nm and 10.6 μm wavelengths might be used depending upon the optical configuration used.

Typically, the laser scan rate will be in the order of 1 to 1000 mm per second with the upper end of this range being limited only by the ability to translate the surface relative to the beam accurately at these speeds and may be increased if suitable equipment is available. In the currently preferred embodiment the scan rate is in the range of 10-500 mm/sec. Laser power and pulse rate must be adjusted in accordance with the scan rate. For continuous (overlapping) grooves, linear scan rates of 44 mm/sec, an average output laser power of 1.5W and a pulse rate of 2.5kHz has been found to be effective. In these circumstances, a chlorine atmosphere having a pressure of one atmosphere has been found to be most effective, however, pressures in the range ¼ atmosphere to 2 atmospheres may be useful under certain circumstances, depending on laser power and scan speed.

In a further preferred form of the invention the groove is cutin an atmosphere comprising a mixture of chlorine and dopant gas whereby surface doping of the groove is performed simultaneously with the cutting of the grooved.

Suitable dopant gases for this process include BCl_3, BF_3, PF_5 and PF_3. At elevated temperatures less volatile dopants such as PCl_3 and $POCl_3$ become useful. In the case of BCl_3, a partial pressure of 0.8 atmospheres in combination with a partial pressure of the chlorine of one atmosphere was found to be effective. In practice, the dopant gas tends to condense when at

optimum concentrations, forming a liquid layer on the surface of the substrate being grooved. This is not undesirable, however, as the laser revaporises the liquid in the region in which the groove is currently being formed and this serves the purpose of concentrating the dopant material in the vicinity of active groove formation.

Description of Preferred Embodiments

Embodiments of the present invention provide methods of forming grooves in silicon material and preferably simultaneously doping the walls of the grooves so formed without the requirement for subsequent etching of the walls of the grooves or the surface of silicon material. Methods in accordance with the invention are particularly useful in the preparation of grooves for buried contact structures in thin film and bulk silicon devices. A possible sequence of steps with which the invention may be used for forming contacts in a thin film silicon device includes:

1. Depositing a multilayer silicon structure and a silicon nitride capping layer by CVD on the glass superstrate or substrate.
2. Laser cutting all the required p-type grooves or craters whilst maintaining a chlorine and BCl_3 atmosphere to effect p-type doping. In this way the grooves do not become contaminated and so the usual wet-chemical groove-cleaning step can be eliminated.
3. Similarly, laser cutting all the n-type grooves while maintaining a chlorine and PF_5 atmosphere.
4. Metallising all the grooves. This can be done easily by electroless nickel and copper plating or alternatively the grooves can be copper plated by CVD.
5. Applying silicon nitride or oxide by CVD over the entire surface to insulate the metallised grooves.
6. Evaporating Al over the entire surface to act as a reflector.
7. Encapsulating the finished module into a protective box.

The example described hereinafter is for the case of laser grooving in which continuous grooves are formed in the surface of the silicon material.

While experiments have shown that simultaneous laser grooving and groove-wall doping, according to the present invention, can be performed with several different types of laser, operating with a broad range of wavelengths and pulse characteristics and using a number of different optical configurations, the best results to date have been achieved with a

pulsed Nd:YAG laser operated with a pulse energy of 0.6mJ at a wavelength of 1064 nm and a repetition rate of up to 40kHz.

In a simultaneous grooving and doping process a relatively large quantity of silicon must be removed to form the groove whilst, virtually at the same instant, a small amount of dopant is incorporated into the wall of the groove. Two mechanisms by which this could occur will be suggested, depending primarily on the wavelength and optical configuration used.

A first requirement when selecting the laser is that the wavelength be strongly absorbed by silicon and, if the silicon is in the form of a thin film on a substrate, weakly absorbed by the substrate. (The grooves go all the way through the silicon to the substrate and laser light absorbed by the substrate might vaporise impurities and contaminate the groove walls). Although the absorption coefficient of crystalline silicon is relatively low for much of the visible and near IR spectrum, liquid silicon absorbs strongly at these wavelengths. The small absorption of high intensity focused laser pulses causes sufficient heating to melt the silicon whereupon the marked increase of the absorption coefficient leads to boiling and ejection of blobs of molten silicon. It has been observed that silicon can be removed to a depth of over 20μm with a single laser pulse by this mechanism.

Lasers may emit either pulsed or continuous wave (cw) radiation. Although focused cw lasers can melt silicon, it is anticipated that only pulsed lasers can achieve the instantaneous peak power densities necessary for ablation or boiling of silicon. Pulsed lasers can be divided roughly into two groups

(i) those producing small pulses (< a few mJ) at high repetition rates (>1 kHz) "cw" Nd:YAG with optional acousto-optical Q-switch (1064 and 532 nm), Cu vapour (510 and 255 nm) and

(ii) those producing large pulses (> 100mJ) at low repetition rates (<100Hz). "Pulsed" Nd:YAG (1064, 532 and 355 nm) excimer (351, 308, 248 and 192 nm).

Lasers belonging to group (i) are suitable for focusing to a round spot, say, 20μm in diameter. Usually the substrate is scanned under the focused spot to scribe a groove. In this case the grooving speed is set by the pulse repetition rate and the depth of silicon removable by each pulse. When spot focusing is used, only lasers capable of removing the full depth of silicon in a single pulse are suitable for grooving at high speeds. For a 20μm

spot with 50% overlap, a 40 kHz pulse repetition rate provides scribing at 400 mm/s. Defocussing of the spot results in the silicon in the groove being melted and dissolved by the reactive gas atmosphere rather that being evaporated and results in more reliable junction formation in heavily doped (eg, $5\times10^{18}cm^{-3}$) semiconductor material.

Lasers belonging to group (ii) are suitable for focusing to a line say $20\mu m$ wide. The length of line is determined by the pulse energy and the fluence required to ablate ($2Jcm^{-2}$) or boil ($150\ Jcm^{-2}$) silicon. For longer wavelength lasers which boil silicon and can be used in single pulse mode, the line is typically a few centimetres long. Short wavelength lasers which need many pulses to make the grooves sufficiently deep might be focussed to a line, or more probably an array of lines, with an overall length of a few hundred centimetres. When line focusing optics are used the grooving speed depends on the laser's power. Speeds of 5 m/s are possible for a 200 W excimer laser.

In addition to expanding or compressing the laser beam in space so as to make the line longer or shorter to optimise the energy density, the pulse can also be extended in duration so that the power density can be optimised. The duration of the laser pulse (its pulse width), plays a key role in determining the depth of silicon removed by each pulse.

The wavelength of the laser emission and the optical configuration used to focus the beam also determine the mechanism by which dopant atoms can become incorporated in the groove walls. In the case of a long wavelength laser removing all the silicon with a single pulse, the residual heat in the groove walls combined with that released in the exothermic reaction between the molten silicon and chlorine, enables the dopant to be incorporated in the silicon before it solidifies. When short wavelength lasers are used many laser pulses are required at every point in the groove. As the high intensity of the pulse is absorbed in the bottom of the groove, thereby making it deeper, radiation of lesser intensity is being absorbed by the groove walls, leading to repeated melting of the walls. Such repeated melting of the walls enables dopant incorporation to occur.

Best results to date, have been achieved using a spot focused Nd:YAG laser at a wavelength of 1064 nm. The results are described in detail below and were achieved with a Directed Light workstation (1995).

Varying Ambient Gas

Laser scribing involves removing material to form grooves. In conventional etching systems, some of the ejected material is sucked away by an exhaust system or blown away by a stream of inert gas and some material remains to contaminate the substrate in the vicinity of the grooves. Such an exhaust system is not suitable for handling the gases necessary for simultaneously doping the walls of the grooves because, the required dopant gases are highly toxic and corrosive, and too expensive to be wasted in this way. Therefore, a completely sealed system is preferred.

In order that the ejected material be prevented from contaminating the surface, it was decided to attempt to react it with the gaseous ambient and form a gaseous product.

When chlorine gas is used as the ambient, a marked reduction in the amount of debris is observed when compared with atmospheric etching. The surface is not only cleaner than for other static ambient cases, but also significantly cleaner and much less oxidised than for the case of exhausted air. Material ejected forcefully and so spending a relatively long time in flight is completely consumed before landing on the substrate. Material ejected less forcefully to the vicinity of the groove continues to react even while in contact with the substrate often being completely consumed and leaving only a burn mark on the surface. These observations are important because they reveal the possibility of achieving simultaneous laser grooving and doping with a Nd:YAG laser where, because of the difficulty of maintaining a stable liquid phase on the surface, little hope was previously thought to exist. The chlorine reacts not only with submicron droplets of silicon, but also with the 5 micron balls and the walls of the grooves. The exothermic nature of the reaction makes it self-sustaining for some time after the laser pulse is finished. Clearly, if Cl_2 can get into the grooves and react with hot silicon, so must a gaseous dopant source. If the quantity of chlorine is enough to consume microns of silicon, the quantity of source gas must be many times that needed for doping.

Varying Cl_2 Pressure

Experiments performed under vacuum and with ¼, ½,1, 1½, and 2 atm of chlorine indicated that pressures below 1 atm produce less cleaning whereas only marginal improvement is observed when the Cl_2 pressure is raised above 1 atm. Even the lowest chlorine pressure of ¼ atm, provides a

substantial absorption of ejected silicon. All further work has been performed under 1 atm of Cl_2 with comparison experiments performed under exhausted air.

Varying Laser Focus

During the course of a single experiment, 28 grooves were cut at varying focusing levels. It was observed that as the laser spot reached its tightest focus, material was ejected with the greatest force and so both the Cl_2 and the exhaust system had their best chance of removing it. For a lens with a focal length of 50 mm, the groove quality starts to degrade noticeably when the deviation from optimum focus exceeded $\pm 200\mu m$. However, as stated above, defocussing the spot can lead to better junction formation and some compromise between groove quality and junction quality can be required for some highly doped materials.

Varying the Distance Travelled Between Laser Pulses

Spot focused optical configurations require a certain amount of overlap between adjacent laser pulses in order to form continuous grooves. Debris accumulation occurs when laser pulses start to overlap, and becomes worse as the overlap increases. Because pulses overlap, ejected silicon impacts upon the walls of the groove already scribed, thus contaminating them with debris. Because some overlap is needed to form a continuous groove, some contamination is inevitable. A line focused optical configuration should prove superior in this respect because in this case the entire groove is produced at the same time, be it by one pulse or many pulses.

Varying the Laser Pulse Energy

Varying the pulse energy indicates that there is an optimum pulse energy which produces the cleanest grooves. If the pulse energy is too low, silicon is not ejected forcefully from the groove and blobs of melted silicon contaminate the walls. If the pulse energy is too high the groove becomes excessively deep and material removed from deep within the bulk silicon wafer has a high probability of impacting the walls. The cleanest grooves are typically 15 to 20 μm deep and 20 to 25 μm wide. The upper bound on the suitable pulse energy can be relaxed when the silicon is in the form of a thin film on a substrate, the maximum depth of the groove being fixed by the thickness of the film.

Varying the Time Interval between Laser Pulses

By varying both the substrate scanning speed and the laser pulse repetition rate it is possible to keep the distance travelled between pulses constant and close to the optimum, while changing the overall grooving speed and the time interval between laser pulses. For each different speed/repetition rate combination used, it is necessary to find an optimum laser power because of the fact that the pulse energy (at constant pump power) varies with the pulse repetition rate. The cleanest grooves are those scribed at the slowest speeds and therefore it is necessary to trade groove quality against speed in deciding the optimum grooving conditions.

Simultaneous Laser Grooving and Doping with Cl_2: Dopant Gas Mixtures Device Fabrication and Characterisation

N-type silicon wafers are thermally oxidised prior to scribing to provide a mask for the substrate surface during subsequent metallisation. Scribing is then performed in a mixture of Cl_2 and BCl_3 as the ambient gas. The addition of BCl_3 to the ambient does not interfere with the removal of the silicon ejected during scribing by reaction with chlorine. A surface contaminating film, produced by the grooving process is removed by RCA cleaning. Such cleaning does not etch silicon and so there is no risk of destroying any groove wall diffusion achieved. After scribing and cleaning, the wafers are annealed under argon at 600°C for 16 hours. Holes are grooved in the rear-surface oxide and a metallic contact consisting of evaporated layers of titanium, palladium and aluminium is deposited. The rear contact is sintered under argon at 400°C for 45 mins. Native oxide is removed from the grooves by treating the front surface with dilute HF solution. Aluminium is then evaporated onto the front surface to make electrical contact to the grooves. The front contact is then preferably sintered. Devices have been made in which the grooves were scribed at different partial pressures of BCl_3 from highest (0.8 atm.) to lowest (0.0 atm.). The partial pressure of Cl_2 was kept constant at 1.0 atm. (Some condensation of liquid BCl_3 occurred when the total pressure exceeded 1.4 atm. but this was not a problem and, by concentrating the source near the surface being scribed, may have been an advantage.) The results show that a substantial and consistent improvement of the turn-on voltage is obtained as the partial pressure of BCl_3 is increased. The optimised turn-on voltage of

about 0.5V compares reasonably well with a turn-on voltage of 0.7V obtained using thermally diffused grooves.

Laser Grooving and Doping at High Speeds

Simultaneous laser grooving and doping have been performed under optimised pitch and power conditions at substrate scanning speeds of up to 400 mm/s. Grooves scribed in pure Cl_2 at high speeds are of poorer quality than those scribed more slowly. In the presence of optimised partial pressures of BCl_3 further speed-dependent degradation of the groove quality occurs. Evidence suggests that laser-pulse-induced condensation of the BCl_3 leads to scattering and distortion of subsequent laser pulses. As the pulse repetition rate increases and the time interval between pulses decreases, scattering and distortion becomes worse because there is less time for the plume of reacting gas and condensate to dissipate. High speed scribing also affected the quality of the diodes produced. By decreasing the table speed and pulse repetition rate by a factor of 8, the turn-on voltage increased by 150 mV and the reverse bias leakage current decreases by a factor of 10 when compared with the best devices scribed at high speed. The problems associated with high speed scanning can be substantially reduced or removed completely if craters are cut instead of continuous grooves.

Laser Grooving and Doping in 0.014 ohm-cm n-Si wafers

Using conditions which optimised the groove-wall diffusion in 0.1 ohm-cm material, compensation of 0.014 ohm-cm ($2x10^{18}cm^{-3}$) n-Si can be achieved. The dark I-V characteristics improve consistently as the partial pressure of BCl_3 is increased.

Laser Grooving and n^+-Doping of p-Silicon

Using gaseous mixtures of chlorine and phosphorus pentafluoride (PF_5) laser scribed grooves in 0.25 ohm-cm ($8x10^{16}cm^{-3}$) p-Si have also been successfully doped n^+-type as determined by the current-voltage characteristics of devices fabricated on the scribed wafers. Grooves scribed in the presence of PF_5 were cleaner than those scribed in pure Cl_2, possibly because PF_5 has two labile F atoms. However, the "Kalrez" O-rings used to seal the gas cell seemed not to be completely inert to the PF_5-containing environment.

Summary of Best Conditions for Simultaneous Laser Grooving and Doping

These are the conditions used to achieve the best simultaneous grooving/doping results obtained to date.

"Directed Light" laser scribing workstation incorporating a "Lee Laser" Nd:YAG laser

Laser Model	815TQ
Operating Mode	TEMøø
Operating wavelength	1064 nm
Pumping lamp power	2.6 KW
Pulse repetition rate	2.5 KHz
Average laser output power	1.5W
Pulse Energy	0.6 mJ
Pulse duration	70 ns
Beam expander	7.5 x
Focal length of objective lens	50 mm
Focus	Optimised for cleanest grooves
Table scan speed	44 mm/s
Partial pressure Cl_2	1 atm
Partial pressure BCl_3	0.8 atm
Temperature	Ambient room temperature
Substrate	0.1 A-cm n-Si wafer with 3500Å thermal oxide

Figures of Merit to the Best Diodes Produced by Simultaneous Laser Grooving and Doping

1. The plot of ln (dark current) versus voltage was linear to c.0.5V giving an ideality factor n=1.9.
2. The slope of the dark current versus voltage curve increased by a factor of $5x10^4$ as the applied bias changed from -1.75 V (reverse bias) to 0.65 V (forward bias).

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

CLAIMS:

1. A method of forming grooves in a surface of a semiconductor substrate or a layered semiconductor material arranged to accept buried contacts, wherein a substrate or layered semiconductor material to be grooved is held in a reactive gas environment at least during a groove cutting process and a laser beam is scanned over the surface of the substrate or layered semiconductor material to cut a groove in the surface of the substrate or layered semiconductor material, the gas pressure, laser wavelength, laser scan rate and peak laser power being selected to optimise groove shape and minimise the amount of debris on surfaces of the substrate or layered semiconductor material and in the groove.

2. A method of forming grooves in a surface and extending through all of one or more semiconductor layers formed on a substrate without significant damage to the substrate, wherein the substrate carrying the layers to be grooved is held in a reactive gas environment at least during a groove cutting process and a laser beam is directed over the surface to cut a groove in the semiconductor layers, the laser wavelength being selected to be strongly absorbed by the semiconductor layers and weakly absorbed by the substrate and laser scan rate and the gas pressure and peak laser power being adjusted to optimise groove formation to control the shape of the groove and amount of debris remaining on the surfaces of the substrate and in the groove.

3. The method of claim 1 or 2, wherein the reactive gas is a halogen or halogen compound.

4. The method of claim 3, wherein the reactive gas is chlorine or a chlorine compound.

5. The method as claimed in any one of claims 1 to 4, wherein the laser wavelength is in the range of 190 nm - 10.6μm.

6. The method as claimed in any one of the preceding claims, wherein the laser is an Nd:YAG laser focused to a spot on the surface to be grooved.

7. The method of claim 6, wherein the laser wavelength is 1064 or 532 nm.

8. The method as claimed in any one of claims 1 to 5, wherein to scribe the grooves, the substrate is translated relative to the beam.

9. The method as claimed in any one of claims 1 to 4, wherein the laser is a high power excimer laser line focused to form lengths of groove.

10. The method of claim 9, wherein the laser wavelength is one of 193, 248, 355, 690 nm or 10.6μm.

11. The method of claim 9 or 10, wherein the substrate is stepped to a new location after each laser pulse so that subsequent groove lengths are formed end on end.

12. The method as claimed in any one of the preceding claims, in which the effective laser scan rate is in the order of 1-1000 mm per second

13. The method of claim 12, wherein the effective scan rate is in the range of 10-500 mm/sec.

14. The method as claimed in any one of claims 1 to 8, wherein the laser wavelength is 1064 nm, the linear scan rate is 44 mm/sec, the average laser output power is 1.5W and the pulse rate is 2.5kHz.

15. The method as claimed in any one of the preceding claims, wherein the substrate is emersed in a chlorine gas environment with a partial pressure in the range ¼ atmosphere to 2 atmospheres.

16. The method of claim 15, wherein the chlorine partial pressure is 1 atmosphere.

17. The method as claimed in any one of claims 1 to 16, wherein grooving is performed in an atmosphere comprising a mixture of chlorine and dopant gas whereby surface doping of the groove is performed simultaneously with the cutting of the groove.

18. The method of claim 17, wherein the dopant gas is selected as one of BCl_3, BF_3, PF_5, PF_3, PCl_3 and $POCl_3$.

19. The method of claim 18, wherein the dopant gas is BCl_3, and is present with a partial pressure of 0.8 atmospheres in combination with a partial pressure of the chlorine of one atmosphere.

INTERNATIONAL SEARCH REPORT

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A.	**CLASSIFICATION OF SUBJECT MATTER**

Int Cl^{6}: H01L 31/18, 21/302, B23K 26/12, 26/16

According to International Patent Classification (IPC) or to both national classification and IPC

B.	**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC: H01L 31/18, 21/302, 306, 3065, 268, B23K 26/12, 26/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT, JAPIO: 1. H01L 31/18, 21/302, 306, 3065, 268 and (LASER) and (GROOVE or ETCH or SCRIBE) and (REACT: or HALOGEN or CHLORINE)
2. B23K 26/12, 26/16 and (LASER) and (GROOVE or ETCH or SCRIBE) and (SEMICONDUCTOR) and (REACT: or HALOGEN or CHLORINE)

C.	**DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 5055696 A (HARAICHI et al) 8 October 1991	
X, Y	Abstract	1, 3-16
Y		2
	US 5139606 A (MAKI) 18 August 1992	
X, Y	Abstract	1, 3-16
Y		2
	US 4624736 A (GEE et al) 25 November 1986	
X, Y	Abstract	1, 5-14
Y		2

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
7 March 1997	15 MAR 1997

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929	I.A.BARRETT Telephone No.: (06) 283 2189

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, Y Y	EP 209288 A1 (BRITISH TELECOMMUNICATIONS PLC) 21 January 1987 Abstract	1, 3-16 2
X Y	Derwent Abstract Accession No. 86-240798/37, Class U11, JP 6-2053731 A (ANRITSU DENKI KK) 17 March 1986 Abstract	1, 3-16 2
X Y	Derwent Abstract Accession No. 84-315360/51, Class P55, JP. 5-9197391. A (HANDOTAI ENERGY KEN) 8 November 1984 Abstract	1, 3-16 2
Y	EP 256938 A2 (DIGITAL EQUIPMENT COPRORATION) 24 February 1988 Abstract	2
A, Y	WO 94/28588 A1 (AMOCO CORPORATION) 8 December 1994 Abstract	1, 3-16
A	GB 2226182 A (PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED) 20 June 1990 Abstract	
A	Derwent Abstract Accession No. 93-147202/18, Class U11, JP. 5-082480 A (HITACHI LTD) 2 April 1993 Abstract	
A	Patent Abstracts of Japan, JP 8-045830 A (HITACHI LTD) 16 February 1996 Abstract	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 96/00831

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	5055696	JP	2062039				
EP	209288	AT	66093	CA	1275613	DE	3680724
		GB	8516984	JP	62018035	JP	6028255
		US	4705593				
EP	256938	CA	1279104	DE	3751551	JP	63134679
		JP	7091661	US	4877480		
WO	9428588	AU	69161/94	AU	663263	EP	651914
GB	2226182	EP	389694	JP	2202022	JP	6082644

END OF ANNEX